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EXPANSION OF THE RAW MATERIALS BASE FOR THE PRODUCTION OF SANITARY WARE CERAMICS

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Investigations have shown that the integrated use of "gornyi" PT pegmatite, granite screenings, and alkali kaolins in porcelain mixes for the production of sanitary ware ceramic decreases the consumption of high-quality quartz-feldspar materials and decreases production costs.

Mixes and adjusting additives which give the required rheological, filtration, and structural-mechanical properties for casting and the prescribed degree of sintering — water absorption $\leq 0.5\%$ in the calcination process at maximum temperature $1220 – 1260°C$ — are used in modern sanitary ware ceramics technology. The following mix compositions ($\%^2$) have been recommended for domestic enterprises: 19 – 22 hydromica – kaolin clays (Novoraiskoe and Veselovskoe), 27 – 30 enriched kaolins (Glukhovetskoe and Prosyanovskoe), 18 – 22 feldspar, 20 – 22 quartz sand, and 6 – 10 porcelain scrap [1, 2].

The use of enriched kaolins and feldspar materials which are shipped from distant locations increases the production costs of ceramic articles. It has been noted that non-enriched alkaline kaolins, granites, and their migmatites can be a promising source of feldspar raw materials [3, 4]. To develop

new mixes it is necessary to take account of the particularities of the composition, properties, and structure formation of the initial components and their mixtures in application to the technology of sanitary ware ceramics.

Granite screenings, pegmatite, and kaolins from the Glukhvetskoe (Vinnitsa oblast'), Oboznovskoe (Kirovograd oblast'), Ekaterinovskoe (Donetsk oblast') deposits, differing by genesis and composition, have been investigated.

According to their genesis, the kaolins from these deposits are primary kaolins and are the final product of the transformations of rock in the process of erosion and hydrothermal action.

According to the chemical composition (Table 1), the non-enriched kaolins — Glukhovitskoe KSSK and Ekaterinovskoe E2013 — belong to the alkaline kaolins subgroup and are distinguished from enriched kaolins by a much higher content of $(K_2O + Na_2O)$ — 4.04 – 5.70 and 1.12 – 1.18%, respectively, and SiO_2, substantially lower content of Al_2O_3 and calcination losses. The compositions of alkaline kaolins from different deposits exhibit their own

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[2] Here and below — content by weight.

TABLE 1.

Kaolin	Content, wt.%									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	calcination losses
Enriched KS-1:										
Prosyanovskoe	44.76	35.06	0.81	0.65	1.53	0.65	1.32	0.65	0.53	13.90
Glukhovetskoe	47.20	36.22	0.32	1.26	0.31	0.22	0.24	0.65	0.47	13.00
Non-enriched:										
Oboznovskoe KO-1	43.53	37.22	0.68	1.16	1.07	0.22	0.72	0.70	0.31	14.40
Glukhovetskoe KSSK	69.48	19.27	0.32	0.33	0.31	0.65	0.17	0.60	3.54	5.25
Ekaterinovskoe E2013	68.90	18.24	0.45	0.21	1.22	0.11	0.31	0.70	5.00	4.80

TABLE 2.

Quartz-feldspar material	Content, wt. %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	calcination losses
KPShM 0.2-2	70.29	15.18	0.17	2.45	0.01	3.10	7.60	0.86
"Gornyi" PT pegmatite	74.05	14.50	0.29	2.35	0.01	2.50	5.25	0.90
Emelyanovskoe granite screenings	69.25	11.97	2.15	3.51	1.76	2.65	5.21	3.00

particularities. For example, the Ekaterinovskoe kaolin E2013 is distinguished from Glukhovetskoe KSSK by a much larger total content of alkaline and alkaline-earth oxides; $(R_2O + RO)$ — 7.0 and 5.1%, respectively. The chemical composition of nonenriched Oboznovskoe kaolin KO-1 is close to that of the enriched type KS-1.

X-ray structural analysis attests to the presence of, together with kaolinite, a substantial quantity of quartz and feldspars, represented by microcline with orthoclase, albite, and mica as impurities, in the composition of the non-enriched KSSK and E2103 kaolins.

However, even with the analogous qualitative mineral composition, the quantitative ratios of the main rock-forming minerals kaolin : quartz : microcline differ substantially: for KSSK kaolin — 1.0 : 1.0 : 0.5 and for of E2013 kaolin — 0.4 : 1.0 : 1.5, i.e., E2013 kaolin is characterized by relatively lower content of kaolinite with a higher concentration of quartz and feldspar.

The analysis shows large differences in the chemical composition of the quartz-feldspar materials (Table 2). It is obvious that the "gornyi" PT pegmatite and granite screenings are inferior to the KPShM 02-2 material ("Kovdor-slyuda," Russian Federation):

with respect to the alkaline oxides $(Na_2O + K_2O)$, comprising 7.8 and 10.7%, respectively;

with respect to the ratio $K_2O : Na_2O$, comprising 1.97 – 2.10 and 2.45, respectively.

On account of the relatively high content (5.27%) of alkaline-earth oxides $(CaO + MgO)$ the granites screenings have the same as the KPShM 0.2-2 material content of $(R_2O + RO)$ oxides — 13.1%.

According to the content of finely disperse particles < 0.001 mm (49.8 – 65.2%) enriched Glukhovetskoe and Prosyanovskoe kaolins of the KS-1 type are of a medium-disperse grade, and according to the total content of particles < 0.01 mm (88.1 – 89.6%) they are highly disperse (Table 3). The KS-1 Prosyanovskoe kaolin differs by the somewhat higher content of finely disperse particles. According to the content of finely disperse particles 0.001 mm (17.2%) and < 0.01 mm (30.0%) KSSK alkaline kaolin belongs to the low-dispersity group. According to the content of particles < 0.001 mm (14.0%) and < 0.01 mm (23.6%) E2013 alkaline kaolin belongs to the coarsely disperse group.

Analysis of the dispersity (content of the most finely disperse particles — < 0.001 mm and < 0.01 mm) has established that kaolins fall into a series:

enriched KS-1 Glukhovestskoe kaolin < Prosvyanovskoe KS-1;

non-enriched E2013 Ekaterinovskoe kaolin < Glukhovetskoe KSSK < Oboznovskoe KO-1.

F. D. Obcharenko and E. G. Kukovskii have performed a large volume of studies of the hydrophilic nature of clays. They attribute the water wettability to the crystal structure of solids, the molecular nature of the surface, and the presence of centers or radicals capable of attaching water molecules to themselves by means of water bonds. However, the initial surface properties of the raw-material components are not really taken into account in practice when determining the rational compositions of the slip mixes for casting sanitary ware ceramics.

TABLE 3.

Kaolin	Content, wt.%, of fractions, mm				
	1.00 – 0.06	0.06 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001
Enriched KS-1:					
Glukhovetskoe	0.17	11.78	9.40	28.80	49.85
Prosyanovskoe	0.40	10.05	8.45	24.95	56.15
Non-enriched:					
Oboznovskoe KO-1	3.18	3.07	3.35	14.85	75.55
Glukhovetskoe KSSK	62.38	7.62	3.00	9.85	17.15
Ekaterinovskoe E2013	70.37	6.08	3.70	5.90	13.95

TABLE 4.

Kaolin	Wetting		Lyophilic factor	Effective specific surface area, m^2/g		Specific surface area, m^2/g
	water	benzene		water	benzene	
Enriched KS-1:						
Glukhovetskoe	0.024	0.194	0.123	35.97	16.99	1.40
Prosyanovskoe	0.058	0.236	0.247	49.64	18.70	1.29
Non-enriched:						
Glukhovetskoe KSSK	0.061	0.145	0.418	19.86	14.30	0.75
Ekaterinovskoe E2013	0.022	0.141	0.153	17.99	14.60	0.52

Experimental data show (Table 4) that with respect to the lyophilic factor all kaolins studied fall into a hydrophilic series:

Enriched KS-1 Glukhovestskoe kaolin < Prosyanovskoe KS-1;

Non-enriched E2013 Ekaterinovskoe kaolin < Oboznovskoe KO-1 < Glukhovetskoe KSSK.

TABLE 5.

Initial component	Content, wt.%		
	type V mix	developed compositions	
		MZTs	VTs5
Clay:			
Veselovskoe VGO-1	12.0	–	–
Vesko-Granitik	–	–	13.60
Vesko-Ékstra	–	2.98	–
Novoraiskoe:			
DN-1	9.0	–	–
DN-0	–	13.05	12.20
Polozhskoe PLG-1	–	9.44	–
Kaolin:			
Glukhovetskoe:			
wet enrichment KS-1	13.0	5.20	6.00
dry enrichment	3.5	–	–
Prosyanovskoe wet enrichment KS-1	4.0	5.20	6.00
Kaolin unenriched:			
Novoselitskoe	9.0		–
Oboznovskoe KO-1	–	8.00	8.00
Raw kaolin non-enriched:			
Glukhovetskoe KSSK	–	16.00	15.00
Ekaterinovskoe E2013	–	14.00	15.00
Quartz-feldspar materials:			
Kondopozhskoe pegmatite	20.0	–	–
KPShM 0.2-2	–	–	8.60
"gornyi" PT pegmatite	–	–	4.50
granite screenings	–	13.13	
Glukhovetskoe quartz sand	20.5	–	–
Porcelain scrap	9.0	13.00	11.10

It is known that the filtration properties of a slip improve as the specific surface area of the raw-material components decreases [5]. In this connection the kaolins studied fall into a series with respect to their filtration power: Ekaterinovskoe E2013 > Glukhvetskoe KSSK > Prosyanovskoe KS-1 > Glukhovestskoe KS-1.

The suitability of clays and kaolins for making sanitary ware ceramics is customarily evaluated on the basis of the flowability of their water suspensions, which is necessary for uniform filling and emptying of molds, with moisture content no exceeding 32 – 33%.

Analysis of water systems showed that suspensions of non-enriched alkaline kaolins fluidize at a much lower moisture content (E2103 — 40.0 – 55.0%, KSSK — 45.0 – 60.0%) as compared with enriched kaolins (55.0 – 75.0%). Suspensions of alkaline kaolins reach the required process flowability in 6 – 7 sec with moisture content 40.0 – 45.0% as opposed to 55.0 – 60.0% for enriched kaolins.

The properties of ceramic articles are associated with their composition and structure. The technological production process is essentially a process of formation and successive transformations of coagulation, condensation, and crystallization structures [6 – 8].

The particularities of the formation of a coagulation structure of slip mixes in the technology of casting ceramics are determined by the stages of the process: interaction of the surface of the particles of the components of the disperse phase with the dispersion medium (water + electrolytes), change of the chemical-mineral and granulometric compositions with the addition of components, partial destruction and change of the rheological characteristics under external pressure during flow into molds, increase of the concentration of the disperse phase during capillary extraction of moisture in gypsum molds or during casting under pressure in polymer molds.

The results of the studies of the chemical and mineral composition, hydrophilic nature, and dispersity of the clay components became the basis for adjusting the mix compositions for producing sanitary ware ceramics (Table 5). In the MZTs and VTs5 mixes, as compared with the V mix, the fraction of clay and kaolin with relatively weaker hydrophilic nature and lower content of finely disperse fractions with a substantial change of the ratio of the fractions of the

enriched and non-enriched kaolins — from 2.3 : 1.0 in mix V to 1.0 : (3.2 – 3.6) in mixes MZTs and VTs5 — were increased successively.

In contrast to the V mix, the quartz-feldspar material KPShM 0.2-2 is completely (MZTs) or half (VTs5) excluded in the mixes developed by integrated introduction of granite screenings, "gornyi" PT pegmatite, and alkaline kaolins and no quartz sand is added.

The chemical compositions of the experimental mixes MZTs and VTs5 differ from the V type by a lower content of SiO_2 and higher content of Al_2O_3 (Table 6).

The MZTs mix differs from the V type as follows:

for the same content of alkaline oxides — 3.75 – 3.76% ($Na_2O + K_2O$), by a higher $K_2O : Na_2O$ ratio — 3.0 versus 1.8;

higher content of alkaline-earth oxides (CaO + MgO) — 1.89 versus 1.40% and total content of oxides of the type ($R_2O + RO$) — 5.65 versus 5.15%.

The VTs5 mix differs from the V type as follows:

higher content of alkaline oxides ($Na_2O + K_2O$) — 4.11 versus 3.75% and substantially higher ratio $K_2O : Na_2O$ — 3.4 versus 1.8;

for the same content of alkaline-earth oxides 1.40 – 1.42% (CaO + MgO) — higher total content of oxides of the type ($R_2O + RO$) — 5.53 versus 5.15%.

The VTs5 mix differs from the MZTs mix as follows:

higher content of alkaline oxides ($Na_2O + K_2O$) — 4.11 versus 3.76% and higher ratio $K_2O : Na_2O$ — 3.4 versus 3.0;

for low content of alkaline-earth oxides — 1.42 versus 1.89% (CaO + MgO) — almost equal total content of oxides of the type ($R_2O + RO$) — 5.53 and 5.65%.

The introduction of non-enriched kaolins into the experimental mixes MZTs and VTs5 substantially changes the total dispersity of the clay components (Table 7). The clay part of the MZTs and VTs5 mixes differs from the V type by a substantially lower content of the finely dispersed particle 0.005 – 0.001 and < 0.001 mm, substantially larger amount of coarsely disperse particles 1.00 – 0.06 mm. In the clay part, the concentration ratio of the fractions 1.00 – 1.06 and < 0.001 mm increases from 0.02 for the V mix to 0.55 for the MZTs and VTs5 mixes, and the mixture of kaolins correspondingly increases from 0.02 to 1.18.

It was determined that the required fluidity depends on the mineral composition and dispersity.

A study of water systems of mixtures of clay initial materials showed that their technological properties depend on the composition and quantitative ratio of the components. The mixture C5 of kaolins corresponding to the composition of the typical V mix was characterized by the ratio of enriched KS-1 and non-enriched KO-1 kaolins 2.3 : 1.0, and the multicomponent mixture 5C corresponding to the experimental compositions of the MZTs and VTs5 mixes differed by the ratio of KS-1 and KO-1 kaolins and non-enriched alkali kaolins equal to 3.0 : 2.0 : 7.5.

It was determined (see Fig. 1) that the fluidity of the suspension increases from 6 to 3 sec for the C5 mixture with the
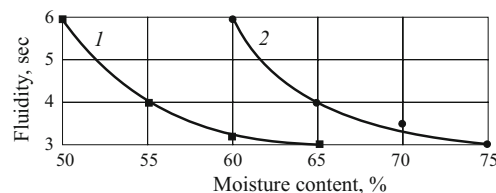

Fig. 1. Fluidity versus moisture content of suspensions of kaolin mixtures 5C (*1*) and C5 (*2*).

disperse phase content decreasing from 40 to 25%, and in the case of the 5C mixture from 50 to 35%. Thus, the water system of a mixture of non-enriched and enriched kaolins 5C reaches the required process fluidity with moisture content 10% lower than a suspension of a mixture of enriched kaolins C5 (at 50 versus 60%, respectively).

In turn, the water systems of mixtures of clays and kaolins of the mixes MZTs and VTs5 (C7, C8) reach the required process fluidity with moisture content 5% lower than in the case of a typical V mix (C6) (60 versus 65%, respectively).

Analysis of the technological properties showed (Table 8) that the slip mixes MZTs and VTs5 as compared with the typical mix V increase the fluidity, and an increase of the casting mass (after 10 min) indicates an improvement of the filtration properties and an increase of the formation rate in the initial cycle.

Sintering during calcination is an important stage in the technology of fabrication of sanitary ware ceramics at which the formation of the structure is completed and the prescribed properties of the articles are attained. Internal pro-

TABLE 6.

Mix	Content, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
V	64.29	22.94	0.62	1.15	0.25	1.34	2.41
MZTs	59.91	25.06	0.97	1.34	0.55	0.94	2.82
VTs5	60.62	25.28	0.65	1.13	0.29	0.94	3.17

TABLE 7.

Mixture (mass)	Content, wt.%, of fractions, mm				
	1.00 – 0.06	0.06 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001
Mixture of clay components					
C6 (V)	1.21	6.07	6.51	20.84	65.37
C7 (MZTs)	27.83	4.85	3.71	12.59	50.98
C8 (VTs5)	27.34	5.48	4.83	14.81	49.30
Mixture of kaolins					
C5 (V)	1.12	8.90	7.42	24.03	58.54
5C (MZTs, VTs5)	40.40	7.22	4.69	13.56	34.13

TABLE 8.

Indicator	Mix		
	V	MZTs	VTs5
Moisture content, %	31.2	30.7	30.5
Density, g/cm³	1.76	1.75	1.75
Fluidity,* sec:			
after 30 sec	5.0	7.0	7.5
after 30 min	12.0	14.0	19.5
Thickening factor	2.4	2.0	2.6
Casting mass after 10 min, g	45.4	52.9	53.7
Casting moisture content, %	19.4	19.3	19.2
Casting thickness after 1.5 h, mm	8.0	8.5	8.5

* An Engler viscosimeter was used.

cesses can occur during sintering: porosity change, crystallization, formation of a liquid phase, spatial redistribution of phases, decrease of the concentration of defects in the crystalline phases, polymorphic transformations of individual phases, chemical reactions in the solid phases and with the participation of the liquid phase, formation of new phases and solid solutions.

It is known that sintering intensifies with increasing temperature and the amount and degree of surface tension of the melt as well as with decreasing particle sizes of the disperse phase. The structure of the melt has predominated over the viscosity.

Low-melting components of ceramic mixes (feldspars, pegmatites, syenites) form during calcination a liquid phase; this activates densification and shrinkage and makes it possible to obtain articles with low porosity and good properties. The formation of a liquid phase during calcination of a ceramic can be regarded as a eutectic melt in the form of thin interlayers due to diffusion of cations of the alkaline and alkaline-earth oxides at the contact sites of amorphous products of decomposition of rock-forming minerals.

The liquid phase plays a dual role during calcination: physical — the separation of particles of the disperse phase decreases as a result of the surface tension of the liquid and chemical — mineral particles dissolve and new crystalline phases, which are thermodynamically more stable at certain temperatures and concentrations, separate from the solution. The reaction rate in the presence of a liquid phase increases substantially with increasing fraction of the eutectic melts and increasing temperature and dispersity of the initial components [9]. The appearance of a liquid phase during calcination of the articles intensifies mullite formation.

A material with the required properties forms during calcination. At temperatures 1040 – 1250°C, sillimanite-like anhydrides are formed first and then mullite and cristobalite form. The viscosity of the melt decreases at temperatures above 1200°C. The separation of the quartz particles and the products of the decomposition of kaolinite as well as mullite crystals decreases at the boundary of the solid and liquid phases under the action of surface tension forces.

Porcelain can be regarded as an example of a composite material where the mullite crystals reinforce the glass phase [10]. The required properties, including heat resistance and strength, of the articles are attained on account of this structure. To decrease the CLTE and increase the heat-resistance of porcelain, it is necessary to obtain a material with the lowest possible content of free quartz and a high content of mullite bound with feldspar glass.

The undissolved quartz and cristobalite crystals decrease the strength of the ceramic material. Their presence in the porcelain manufacturing process can result in the production of internal stresses and microcracks as a result of changes in the volume of an article during cool-down in the furnace. In this connection, it is important to note that according to x-ray structural analysis the crystallization structure of sanitary ware ceramic made from the MZTs and VTs5 mixes after calcination in a tunnel furnace at maximum temperature 1220°C shows the same degree of mullite formation as the material made from V mix with a much lower content of quartz which does not dissolve in the melt.

Construction porcelain made from the mixes developed is characterized, after firing in a tunnel furnace at the maximum temperature 1220°C, by the required degree of sintering (water absorption 0.2 – 0.3%, density 2.27 – 2.30 g/cm³, open porosity 0.4 – 0.7%), which gives sanitary ware ceramic articles that meet the operative standards.

Integrated introduction of non-enriched alkaline kaolins from the deposits in Vinnitsa and Donetsk oblast's and 10 – 15% granite screenings from the deposits in the Zhitomir oblast' gives with the maximum calcination temperature 1220°C a high degree of sintering of the porcelain paste (specific closed-pore fraction 90.3%, density 2.30 g/cm³) and the required physical – mechanical properties (water absorption 0.18%, bending strength 39 – 40 MPa).

In summary, integrated utilization of "gornyi" PT pegmatite, granite screenings, and alkali kaolins in a porcelain mix for the production of sanitary ware ceramic makes it possible to decrease the consumption high-quality quartz-feldspar materials and decrease the production costs.

The rheological properties of suspensions of MZTs and VTs5 kaolin mixes are improved as compared with the typical mix by regulating the quantitative ratio of the enriched and non-enriched kaolins. The improvement is due to a decrease of the number of contacts between particles and the viscosity with a 24% decrease of the content of finely disperse particles (< 0.001 mm) and a 39% increase of the number of coarsely disperse particles (1.00 – 0.06 mm).

The rheological and process properties of slips from MZTs and VTs5 mixes can be increased by adjusting the qualitative composition and quantitative ratio of the clays, enriched and non-enriched kaolins; the effect is due to a decrease of the number of interparticle contacts and the viscosity of their clay component with a 14 – 16% decrease of the content of finely disperse particles (< 0.001 mm) and a 26%

increase of the number of coarsely disperse particles (1.00 – 0.06 mm).

The crystallization structure of the sanitary ware ceramic prepared from the mixes developed with relatively lower initial content of kaolinite as compared with the typical porcelain mix is characterized by an equal degree of mullite formation, which is due to the structural imperfections and the high reactivity of the rock-forming minerals of alkali kaolins as well as the development of quartz-feldspar glass phase.

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